Indian J. Phys. **82** (11), 1513-1522 (2008)

UV-visible-near IR and infrared spectroscopy of β-carotene and β-carotene-iodine complex

A T Oza*, G K Solanki, Anand Amin and Parimal Trivedi

Department of Physics, Sardar Patel University, Vallabh Vidyanagar 388 120, Gujarat, India

E-mail ajayozat@yahoo.com

Received 15 October 2007, accepted 22 July 2008

Abstract β-carotene which a well known precursor of vitamin A forms a charge transfer complex with iodine β-carotene and its iodine complex both are studied with ultraviolet- visible- near infrared and mid-infrared spectroscopy The spectra are analyzed for the nature of transitions and free-carrier absorption β-carotene -iodine shows a broad and intense Gaussian band around 400 nm Band assignments of the infrared spectra are also carried out The first derivative profiles are also plotted

Keywords · Ultraviolet-visible spectroscopy, infrared spectroscopy, β-carotene, electronic transition, Gaussian bands

PACS Nos. · 78 30 JW, 87 15 Mi, 71 20 Ni

1. Introduction

β-carotene is extracted from carrot and is a well – known precursor of vitamin A [1] It is a semiconductor as well as photonconductor [2,3]. Here it is our interest to study how optical properties of β-carotene changes under complex formation with iodine. Optical absorption and electrical properties are related [4]. Therefore, we study β-carotene and β-carotene-iodine complex with UV-visible near IR as well as IR spectroscopies between 200 nm and 1600 nm and 400-4000 cm^{-1} range respectively.

2. Experimental

β-carotene was obtained from Sigma chemical company which was analytical reagent and therefore, about 99% pure. β-carotene was grinded in a mortar to make it a

Corresponding Author

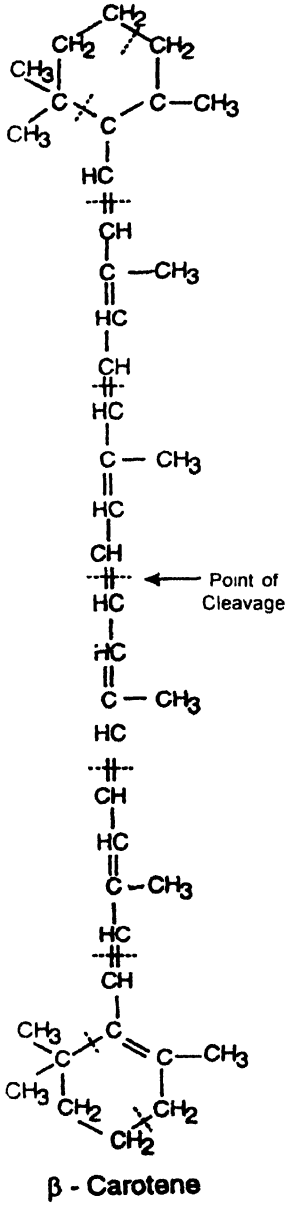

Figure 1 Molecular structure of β -carotene

microcrystalline powder and pasted on a visible transmitting strip with paraffin oil It was placed in a standard spectrophotometer of Perkin-Elmer Company to record the spectrum in the range 200-1600 nm β -carotene and iodine were mixed in 1 1 molecular weight proportions and grinded in a mortar till the colour changed due to the formation of charge transfer complex The same process as in the case of β -carotene was followed for recording UV-visible-near IR spectrum Molecular structure of β -carotene is shown in Figure 1

The infrared spectra (KBr mull) of β -carotene and β -carotene-iodine (1 1) complex in the range 400-4000 cm^{-1} were obtained using a GXFTIR single beam spectrophotometer of Perkin-Elmer Company, U S A It had resolution of 0 15 cm^{-1} scan range 15,600 – 30 cm^{-1} scan time 20 scan/sec and OPD velocity of 0 20 cm/sec MIRTGS and FIRTGS detectors were used

2. Results and discussion

The UV-visible – near IR spectra of β -carotene and its iodine complex are shown in Figures 2 and 3 In the β -carotene spectrum, one band is found at 300 nm A sharp drop in absorption is found at 500 nm Above 600 nm, the transmission becomes almost constant upto 1600 nm Three weak (compared to background) absorption bands are visible at 1170 nm, 1230 nm and 1350 nm There is also an absorption band at 750 nm and a plateau in transmission in the range 1400-1600 nm The spectrum of iodine (Figure 3) shows a rise in transmission of 300 nm band from 21% to 77 5% There is a monotonic rise in transmission above 580 nm and broad and intense band at 1000 nm Absorption bands in the spectrum of β -carotene at 1170 nm 1230 nm and 1350 nm show red shift The absorption bands in the spectrum of β -carotene shift to 1170 nm, 1230 nm, 1300 nm and 1420 nm in the iodine complex Absorption at 380 nm, 430 nm and 450 nm develop in the spectrum if iodine complex which are not at all observed in β -carotene spectrum

The infrared spectra of β -carotene and β -carotene-iodine are shown in Figure 4 in the range 400-4000 cm^{-1} Several bands arising from characteristic vibrations of β -carotene are observed and broaden and split in the iodine complex This shows that iodine leads

to delocalization of charge carriers. The photoconductivity most probably arises from the absorption edge in the infrared range at 1900 cm^{-1} in β-carotene This somewhat reduces to 1800 cm^{-1} in the spectrum of iodine complex.

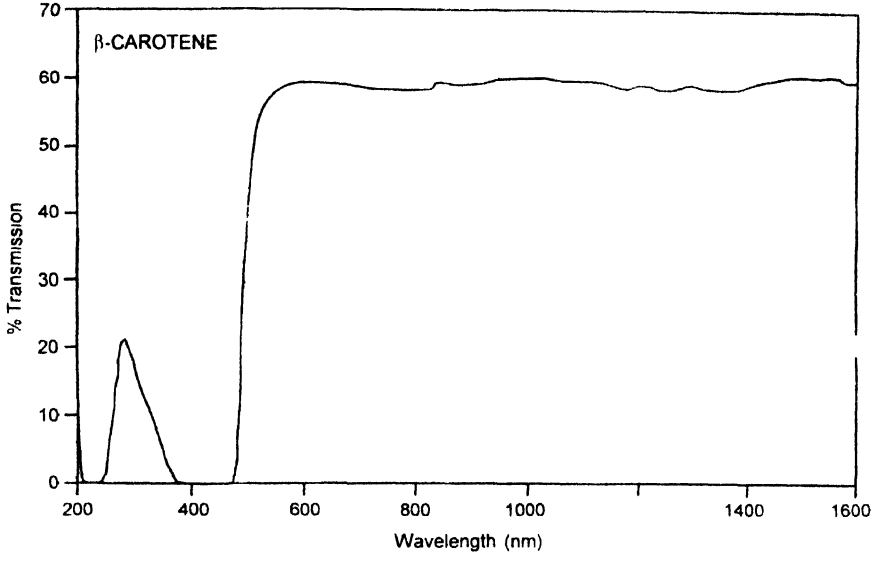

Figure 2. UV-visible near IR spectrum of β-carotene.

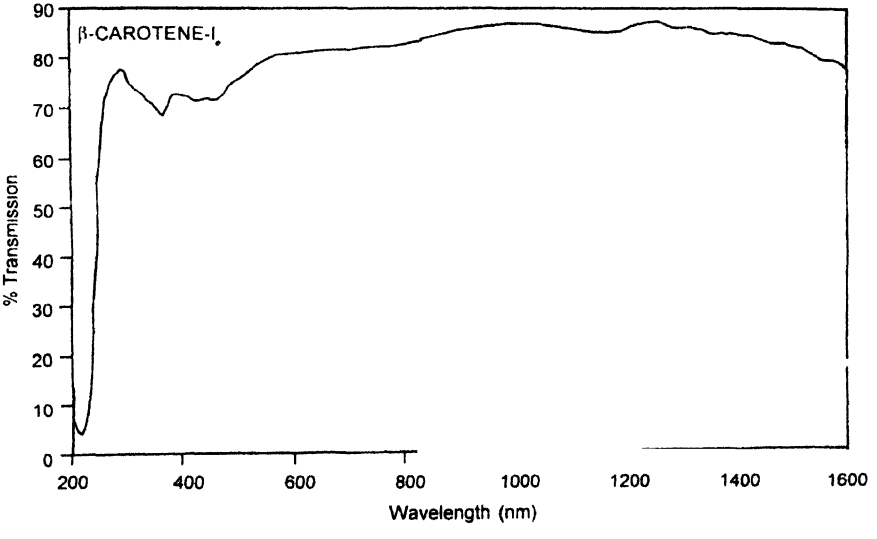

Figure 3. UV-visible near IR spectrum of β-carotene-iodine (1 1) complex.

4. Analysis and interpretation

The strong band in transmission of β-carotene at 300 nm can be ascribed to $\sigma \rightarrow \pi^*$ transition. This transition is most affected by its interaction with iodine and the transmission of transition rises about 21% to 77.5% in iodine complex. The optical absorption edge of

β -carotene occurs around 2 4 eV (500 nm) (hindered cis-isomer) because β -carotene is a semiconductor A comparative graph of β -carotene and its iodine complex is shown in

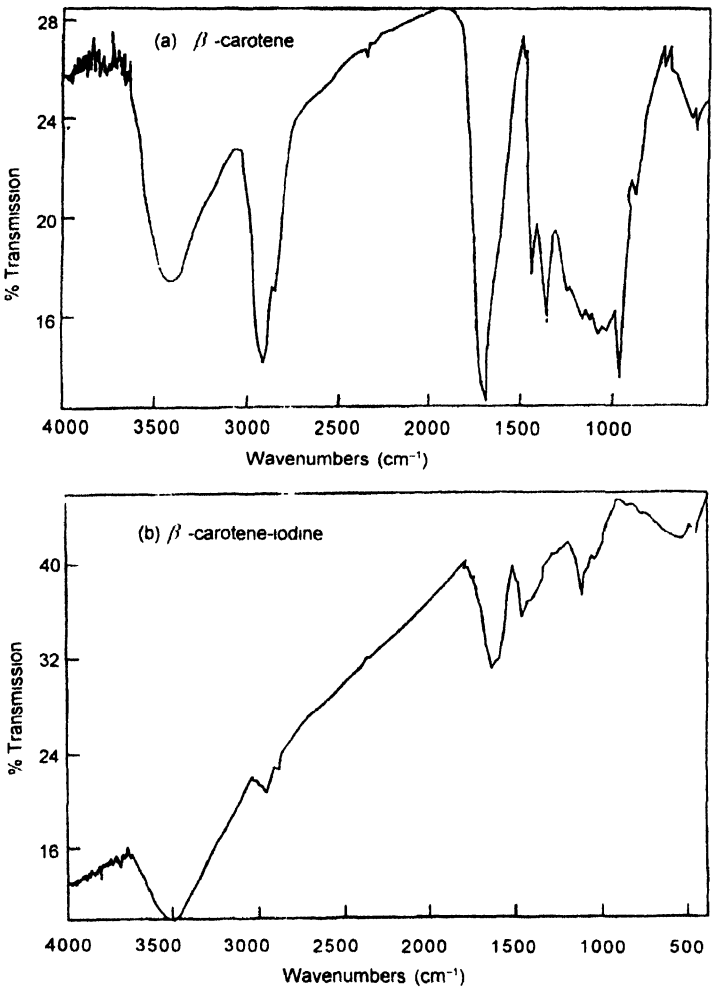

Figure 4. Infrared spectra of (a) β -carotene and (b) β -carotene-iodine

Figure 5. The iodine complex reveals a broad Gaussian absorption band around 400 nm (3.0 eV) and optical absorption edge of β -carotene is wiped out The Gaussian distribution is a smooth approximation; otherwise it is absorption shape of the real part of dielectric constant around 340 nm

The optical absorption edge of β -carotene reveals itself as a rise in transmission at 500 nm. The edge is analyzed to fit the relation [4]

$$Ahv = B\left(hv - E_g\right)^{1/2}$$

which is the absorption (A) for a direct allowed transition in a disordered material In Ahv *vs* ln (hv–E_g) is plotted (Figure 6a) and slope is found to be ½ After this verification,

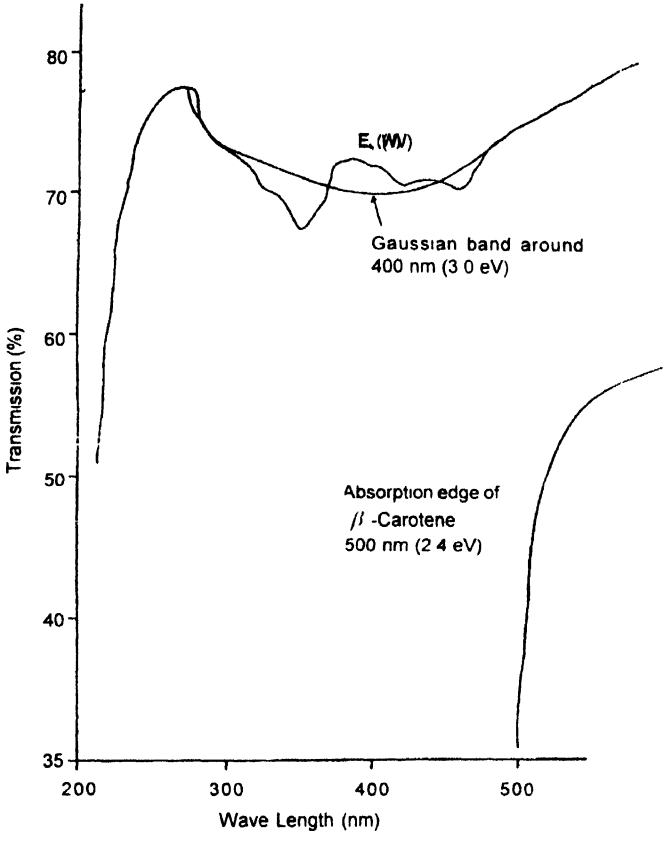

Figure 5 A comparison of absorption edge of β-carotene with spectrum of the iodine complex

$(Ahv)^2$ *vs* hv is plotted (Figure 6b) which is found to be a good straight line having an intercept on x-axis E_g = 2 0 eV (600 nm) This shows that it is a direct allowed transition across a band gap between the top of the valence band and the bottom of the conduction band

Next is the analysis of free-carrier absorption in the conduction band region, *i.e* $hv > E_g$ [5] Log A (A in %) *vs* log λ (λ in nm) is plotted for this purpose (Figure 7) because it is supposed to obey a power law The slope is 1 8 showing the relation

$$\alpha_f = A\lambda^{1\,8}$$

i e the power (exponent) is 1 8 This shows that the charge carriers are scattered by acoustic phonons [6]. The phonons do not play role in the transitions across the band gap but do scatter free charge carriers

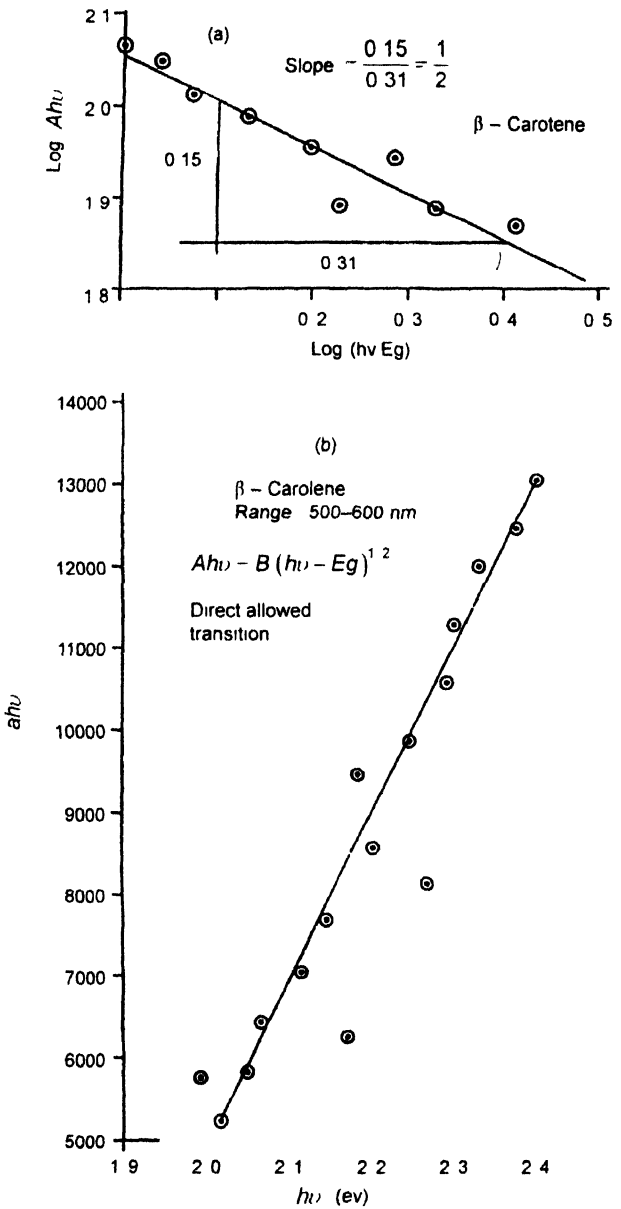

Figure 6 Nature of transition of β-carotene which is a direct allowed transition

A broad absorption band around 775 nm can be due to delocalization of charge carriers along the long β carotene chain Three absorption bands at 1170 nm, 1230 nm and 1350 nm can be assigned to the spin-orbit splitting of valence band [4] The gaps among triply split band absorb electromagnetic radiation This triplet is red shifted to 1180 nm 1300 nm and 1470 nm in the iodine complex This can be due to band tailing effect in a charge transfer between β-carotene and iodine

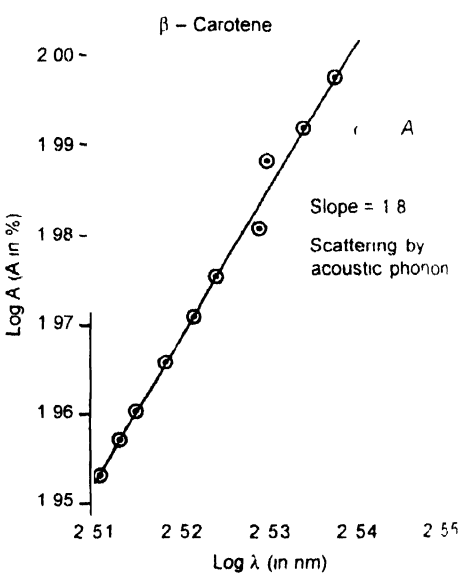

Figure 7 Free-carrier absorption in β carotene This shows scattering of charge carriers by acoustic phonons

The enlarged diagram of the Gaussian envelope in the spectrum of β-carotene-iodine complex is shown in separately (Figure 8a) and it is fitted the relation (Figure 8b)

$$A = A_0 \exp\left| \frac{(\lambda - \lambda_0)^2}{2M_2} \right.$$

which is the Gaussian distribution where M_2 is the second – moment of the distribution This reveals that there is density of states having Gaussian distribution within the forbidden energy gap. The Gaussian curve is somewhat asymmetric having long wavelength tail.

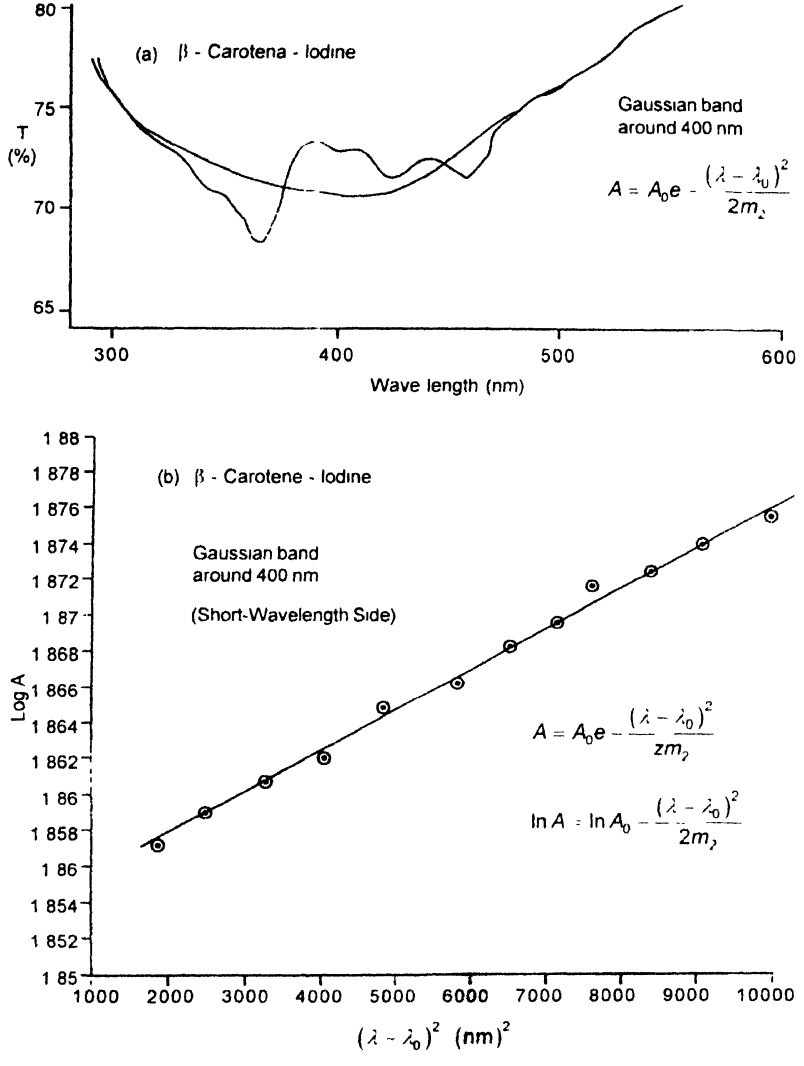

Figure 8. Gaussian envelope of absorption in β-carotene- iodine and its Gaussian distribution fit.

In the spectrum of β-carotene-iodine complex, there are weak absorption bands at 380 nm and 450 nm which are not found the spectrum only β-carotene. This can be related to electronic excitation induced by iodine in the long hydrocarbon chain of β-carotene. There is a monotonic rise in transmission above 580 nm which follows an intense transmission band around 1000 nm. This can be ascribed to a change in dielectric constant of β-carotene due to its complexation with iodine.

The band at 775 nm in β-carotene spectrum is replaced by a plateau in the spectrum of the iodine complex Similarly there is a plateau in transmission in β-carotene in the range 1400-1600 nm while there is an absorption band in this range in β-carotene-I_2 spectrum This inverted behaviour shows that there is a borrowing of oscillator strength from the band at 775 nm in β-carotene At 775 nm, β-carotene shows an absorption band and the iodine complex shows a plateau while around 1550 nm β-carotene shows a plateau and the iodine complex shows an absorption band This occurs at approximately half energy This band at 1550 nm for iodine complex is a charge transfer band Thus the delocalization of charge carriers along β-carotene chain gets transferred to iodine when complex formation occurs

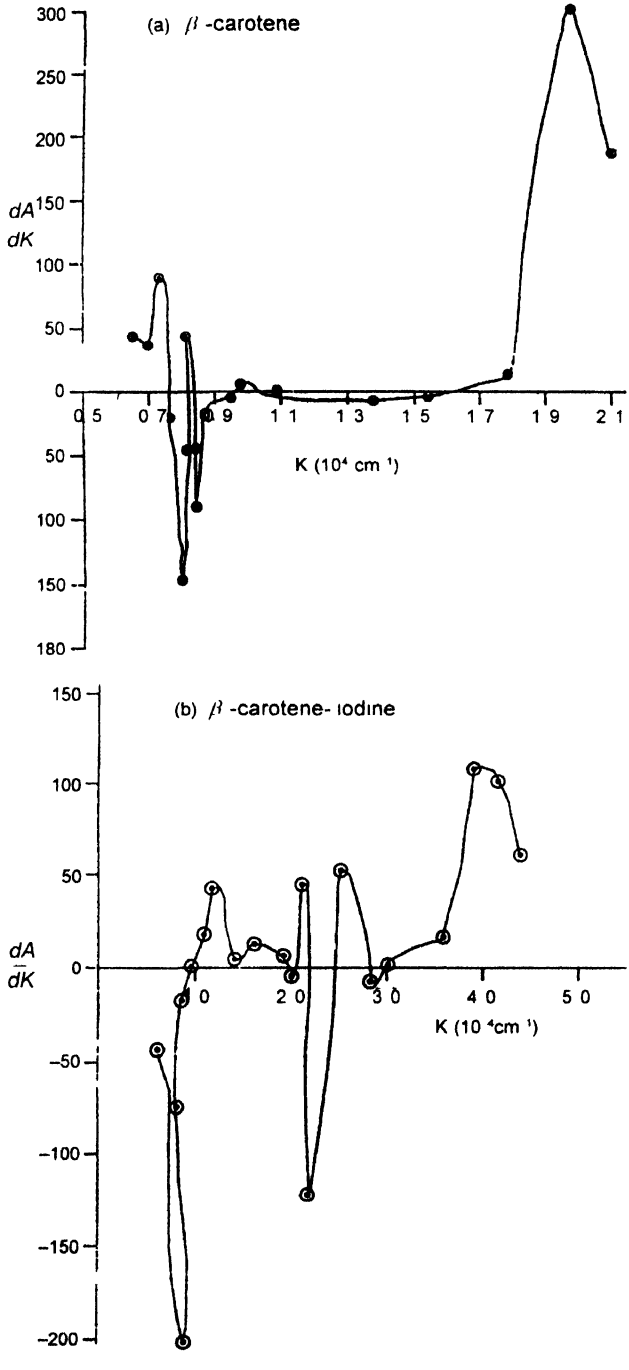

Figure 9 First derivative of spectra of (a) β-carotene and (b) β-carotene- iodine

For better resolution, the first derivative spectra are plotted (Figure 9) The zeros of the first derivative mark the position of broad bands The red-shifting of these absorptions is due to the interaction of β carotene and iodine which leads to the broadening of spin orbit split bands of valence band, *i e* one type of band tailing reducing the energy gaps among three parts of the valence band There is a triplet between 1 eV and 2 2 eV with centre band diminished in the spectrum of β-carotene-iodine (Figure 9b) It is absent in the spectrum of β-carotene (Figure 9a) This proves that iodine excites and interacts with several methyl groups

on β-carotene molecule The nature of transition and free carrier absorption in the spectrum of β-carotene-iodie complex are also analyzed (Figure 10) Acoustic phonons scatter charge carriers but a direct transition in β-carotene becomes indirect in β-carotene-iodine complex

Next is regarding the infrared spectra of β-carotene and its iodine complex The absorption edge found at 0 225 eV is the infrared spectrum of β-carotene can be considered as a Peierls absorption edge due to Kuhn periodicity or a Peierls distortion along chain of β-carotene (Figure 11) This band gap reduces to 0 20 eV in β-carotene-iodine band gap by only phonon energy The infrared absorption edge in β-carotene and its iodine complex reveal indirect forbidden transitions

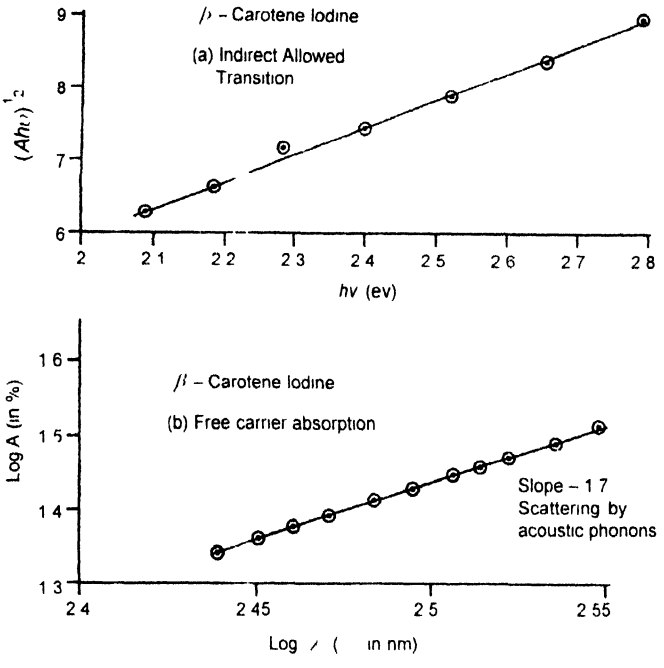

Figure 10 (a) Nature of transition in β carotene-iodine and (b) free-carrier absorption in β-carotene- iodine

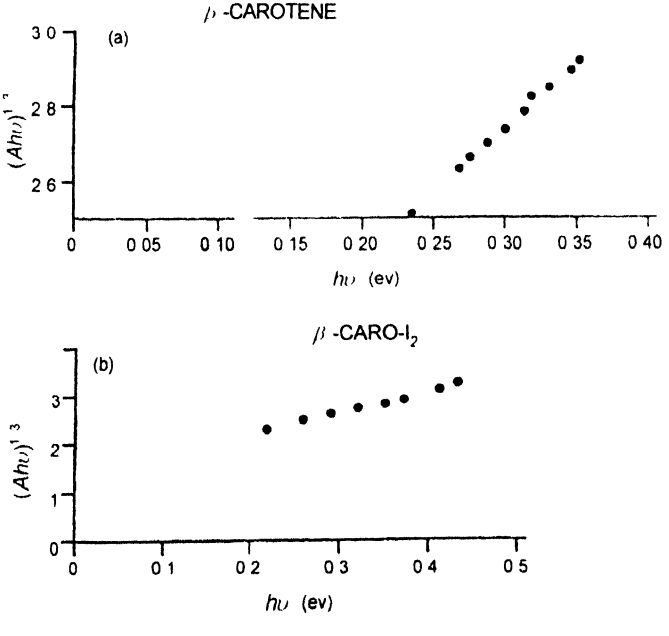

Figure 11. Infrared absorption edges of (a) β-carotene and (b) β-carotene- iodine which both shows an indirect transition which is forbidden

5. Conclusions

Iodine dissociates 300 nm exciton of β-carotene molecule by Gaussian forces Iodine creates Gaussian absorption above the gap region of β-carotene Iodine reduces the gaps among the spin orbit split valence band and lowers the frequencies of interband transitions There is

a borrowing of oscillator strength from 750 nm band in β-carotene spectrum for the development of charge transfer band at half-energy, *i.e.* 1550 nm in the spectrum of iodine complex. Iodine changes a direct transition in β-carotene into an indirect transition in β-carotene-I_2 complex. The infrared gap is also reduced gap by iodine, although by a small amount of the order of phonon energy.

References

[1] A L Lehninger *Principles of Biochemistry* (Delhi, India CBS Publishers & Distributors) (1984)

[2] F Gutman and L E Lyons *Organic Semiconductors* (New York · John Willey and Sons) (p 758 778) (1967)

[3] D D Eley *In Organic Semiconducting Polymers (Ed)* J E Katon (Marcel Dekker Co.) (1968)

[4] J I Pankove *Optical Processes in Semiconductors* (Englewood Chiffs, New Jersey Prentice Hall Inc) (1971)

[5] P S Kireev *Semiconductor Physics* (Moscow · Mir Publishers) p. 515 (1975)

[6] Y Fan, W G Spitzer and R J Collins *Phys Rev.* **101** 566 (1956)